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Laboratory
Las Vegas NV 89114

Research and Development

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Project Summary

Remote Monitoring of Organic Carbon in Surface Waters

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Results of this laboratory feasibility study show that the intensity of the Raman normalized fluorescence emission induced in surface waters by ultraviolet (UV) radiation can be used to provide a unique airborne remote sensing capability for monitoring the concentration of dissolved organic carbon (DOC). Trace concentrations of hydrocarbons, both man-made and natural in origin, are the predominant source for this fluorescence. Water, on the other hand, is nonfluorescent under UV irradiation, but emits an intense Raman band of constant amplitude relative to the incident light. This Raman emission can be used as an internal reference or normalizing standard with which to correct the fluorescence emission for the effects of attenuation, for variations in system sensitivity, and for changes in sensor elevation. It is recommended that a direct calibration of the airborne fluorescence data in terms of equivalent DOC concentration be accomplished by making DOC measurements on samples obtained at a small number of reference sites under the aircraft flight path at the time of the airborne survey.

Airborne laser fluorosensors that utilize this principle will provide a synoptic survey capability for rapidly and cost effectively producing isopleth maps that show concentrations of surface water DOC. These concentrations can be used for delineating gradients, temporal changes and anomalies in the distribution of total dissolved organics in the surface layers of rivers, lakes and coastal waters. Anomalous features in the airborne data that cannot be readily explained on the basis of existing information can then be investigated in more detail either by means of *in situ* monitoring or by laboratory analyses of grab samples. Specific applications will include collecting baseline data, verifying lake cleanup and restoration, designing sampling networks, modeling ecosystems and locating point and nonpoint sources of unknown origin. Sources of organic carbon include, but are not restricted to, harbors, marinas, septic tank leachates, oil refineries and industrial sites adjacent to waterways, pulp and paper mill effluents, feed lot runoff, municipal sewage effluents, agricultural and silviculture activities, and surface runoff containing organic materials from both living and decayed natural vegetation.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Total organic carbon (TOC) and DOC determinations are routinely accom-

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plished by making laboratory analyses on grab samples. This approach is both time-consuming and costly in terms of manpower and facilities. In addition, because of the relatively long time required to take grab samples from launches or helicopters, it is rarely possible to obtain a synoptic record of organic carbon distribution for a given water surface due to water movement and diurnal effects. In contrast, both airborne and satellite remote monitoring techniques are capable of rapidly and cost effectively providing data for certain water quality parameters from large areas of water surface without influencing the nature of the sample.

The subject of this laboratory study is the feasibility of measuring the concentration of organic carbon in the surface layers of natural waters from an airborne platform. At the present time, no proven remote sensing technique exists that is capable of monitoring, directly or indirectly, the organic carbon content of surface waters. It is therefore intended that the results of this study will be used to establish criteria for the design of a compact integrated airborne system capable of mapping trends, gradients and anomalies in the distribution of organic carbon in surface waters. An investigation of the relationships between the fluorescence characteristics of surface waters and the widely accepted organic carbon water quality parameters, TOC and DOC, was therefore made with the purpose of establishing the feasibility of using the fluorescence signature as a remote sensing indicator of total organics in surface waters. In particular, attention was paid to finding the best water fluorescence parameter for this purpose and to investigating the merits of the Raman normalization procedure as a means of correcting both the laboratory and airborne measured fluorescence data for the effects of optical attenuation.

Effects of Optical Attenuation on Water Fluorescence Measurements

Airborne laser fluorosensors use high power, pulsed, blue or ultraviolet lasers to excite fluorescence emission in a sample volume in the water surface. A fraction of this multidirectional emission is collected by a large aperture telescope and converted into an electrical signal by an optical detector. The principle of operation for the laser fluorosensor is illustrated in Figure 1 in which the airborne platform is usually flown at a height of several hundred meters above the water surface. The volume of water interrogated by the system is approximately defined by the diameter of the laser excitation spot on the water surface and the penetration depth of the laser beam. This fluorescense emission signal, in conjunction with aircraft navigation data, can be used to prepare isopleth maps showing the variation in concentration of the specific water quality parameter under investigation as illustrated in Figure 2.

The spectral nature of this laser induced fluorescence emission from typical surface waters can be readily demonstrated using a proprietary laboratory spectrofluorometer. The two emission spectra, shown in Figure 3, were obtained on high purity and lake water samples using a laboratory-corrected spectra spectrofluorometer.

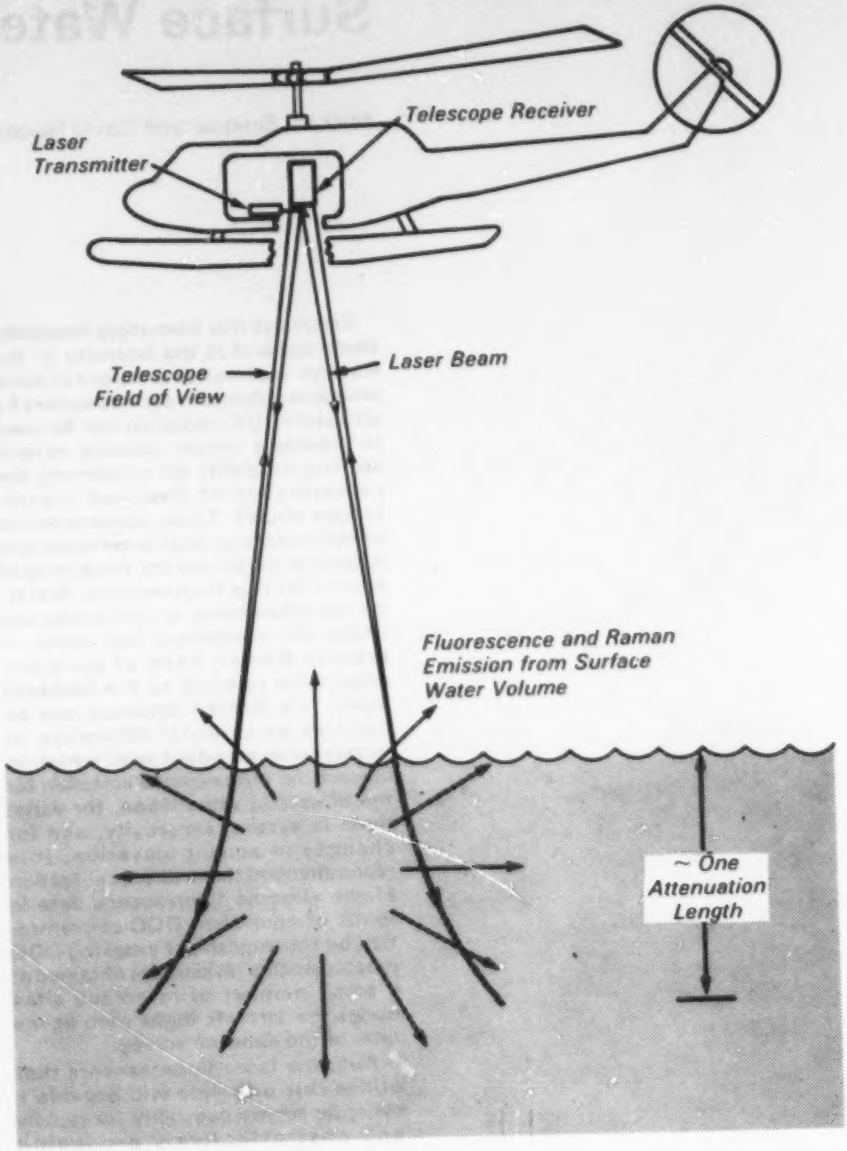

Figure 1. Principle of operation of airborne laser fluorosensor.

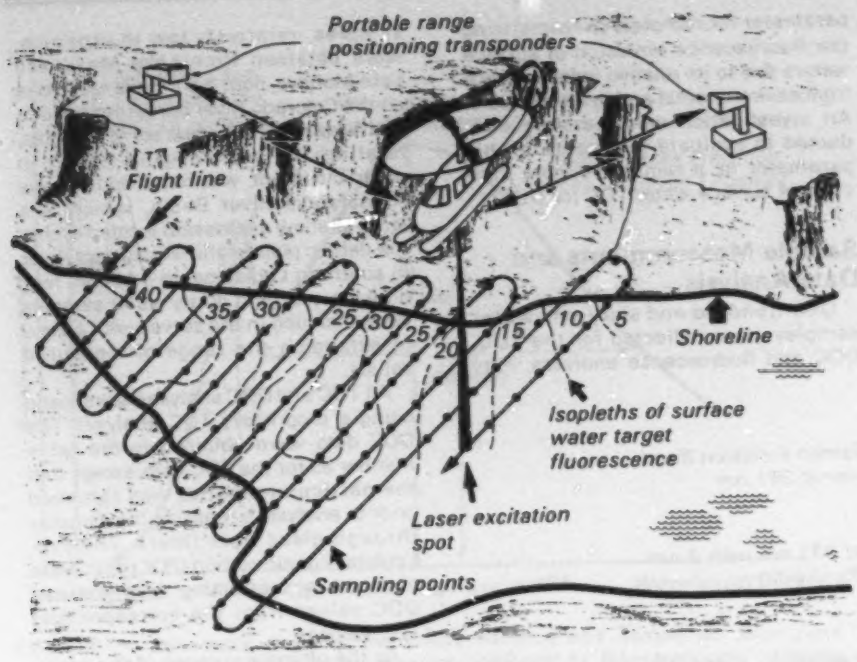

Figure 2. Schematic illustrating possible mode of operation of an airborne laser fluorosensor for mapping surface water distributions of DOC.

Excitation at 337 nm was employed as it lies close to the wavelength producing the maximum fluorescence emission in water samples and also because it corresponds to that of the widely available pulsed nitrogen laser. These water fluorescence spectra exhibit two features of interest. First, the lake water sample exhibits a broad blue fluorescence band peaked in the region of 430 nm whereas the spectrum for the high purity sample is essentially fluorescence free. The sample obtained from Lake Mead in Nevada, is known to be low in organics, having a TOC level on the order of 1 mg/l. This suggests that a fluorescence signal that can be measured with high sensitivity from samples low in TOC might be usable as an indicator of surface water organics, provided that the fluorescence and organic carbon parameters can be related in a meaningful way.

The other spectral feature, an intense, relatively narrow, constant amplitude band located at 381 nm and superimposed on the fluorescence spectrum, is the Raman emission for the OH vibrational stretching mode of water. For high purity samples or those relatively low in dissolved and particulate matter, e.g., most drinking waters, and for a constant excitation intensity, the amplitude of the Raman signal emitted from a short (1 cm) pathlength sample remains essentially constant. However, in the presence of more significant concentrations of dissolved and particulate matter, the intensity of this Raman signal will be attenuated by absorption and scattering losses. In the case of the fluorescence signal, changes in intensity may be due either to this optical attenuation or to changes in concentration of the fluorescent substances under investigation thereby introducing ambiguities into the interpretation of the fluorescence data. This attenuation can be significant in the case of samples high in dissolved organics with the result that the attenuated fluorescence signal will indicate a lower value of TOC than is actually present.

In a laboratory setting, significant attenuation of the fluorescence emission due to self-absorption can occur for 1-cm thick samples that contain high levels of organics. In an airborne laser fluorosensor application, the effective volume of sample being interrogated will depend critically on the penetration depth of the laser beam through the surface water. As this depth or attenuation length may vary over a range of 100 to 1 or more for a given water body, very large errors can be incurred in the measured fluorescence signal. Consequently, as the Raman signal is a property of water alone, and as the concentration of water is constant for all but grossly polluted waters, observed variations in its intensity will be due to variations in the optical attenuation coefficients at the laser and Raman wavelengths. The Raman signal can therefore be used as an internal reference standard with which to monitor the effect of changes in these attenuation coefficients on the concurrent fluorescence signal.

By taking F_λ/R, the ratio of the fluorescence emission intensity, F_λ, at any wavelength, λ, to the corresponding Raman value, R, whether measured from an airborne platform or in the laboratory, a parameter is obtained that, to a first approximation, varies only as the concentration of the homogeneously distributed fluorescent organics and is independent of changes in the optical attenuation coefficients at the laser (excitation), fluorescence and Raman wavelengths. Use of this Raman correction technique has recently been successfully demonstrated by the present authors in a similar airborne remote sensing application, which involved monitoring the concentration of surface water chlorophyll *a*.

In applications to remotely monitor the concentration of total organics, three significant advantages are to be gained by normalizing the fluorescence signal with the concurrent water Raman signal:

(i) Raman normalization corrects for the attenuation of the fluorescence signal due to the presence of either inorganic or organic particulate and dissolved matter.

(ii) Raman normalization of the fluorescence data eliminates problems due to changes in system sensitivity, in particular those involving laser output power, provided that these changes have an equal influence on both the fluorescence and Raman signals.

(iii) As both the fluorescence and Raman signals exhibit a $1/H^2$ dependence on changes in

aircraft altitude, H, above the water surface target, the ratio F_λ/R is independent of these changes.

It should be mentioned that (i) and (ii) apply equally to remote sensing, *in situ* or laboratory applications for measuring water fluorescence, although for (i), attenuation effects in 1-cm pathlength samples will be relatively small, requiring corrections to the fluorescence signal no greater than 50 percent.

Based on the above observations, the fluorescence to Raman ratio, F_λ/R, would appear to be an ideal candidate parameter for remotely characterizing the fluorescence emission of surface waters due to its relative independence from environmental and system factors. An investigation was therefore conducted to evaluate the merits of this parameter as a remote sensing indicator of surface water TOC (or DOC).

Sample Measurements and Data Analysis

One-hundred and sixty-one water samples were collected for the TOC, DOC and fluorescence analyses. Fifty samples, relatively low in organics, were obtained from Lake Mead and Lake Mohave, both man-made reservoirs on the Colorado River bordering Arizona and Nevada. The largest set of samples, totaling 107 and ranging widely in organic content, was obtained from the Atchafalaya River Basin, which is a large shallow depression located within the deltaic plain of the Mississippi River in southern Louisiana. In addition, four drinking and high purity water samples were included in the survey with a view to extending the range of measured values.

All TOC and DOC analyses were made using a proprietary TOC analyzer. The DOC data were obtained in the same manner as for the TOC data except that the particulate matter was removed prior to analysis by passing the samples through glass fiber filters. The particulate organic carbon (POC) data were obtained by subtracting the measured DOC values from the corresponding TOC values.

As the ultimate purpose of this feasibility study is to establish a method for remotely measuring the concentration of total organics for *in situ* surface water samples using fluorometric techniques, every effort was made to ensure that the grab samples for fluorescence analysis remained as representative of the true field conditions as was practicably possible. Clearly, remote sensing operations do not allow for any form of sample preparation or conditioning. Extensive precautions were therefore taken to ensure that the integrity of the fluorescence properties of the grab samples was maintained during the period between collection and analysis.

All fluorometric measurements were made using a proprietary spectrofluorometer capable of producing fluorescence spectra on a relative quanta scale that have been corrected for the spectral artifacts introduced by the xenon excitation lamp, the excitation and emission grating monochromators and the photomultiplier detector.

Water fluorescence emission spectra, as typified by those shown in Figure 3, were obtained by exciting the sample at 337 nm and scanning the emission spectrum from 350 nm to 500 nm. A fixed excitation wavelength of 337 nm was employed throughout this study primarily because this wavelength was found to be close to that producing the maximum fluorescence emission from fresh water samples. A fluorescence

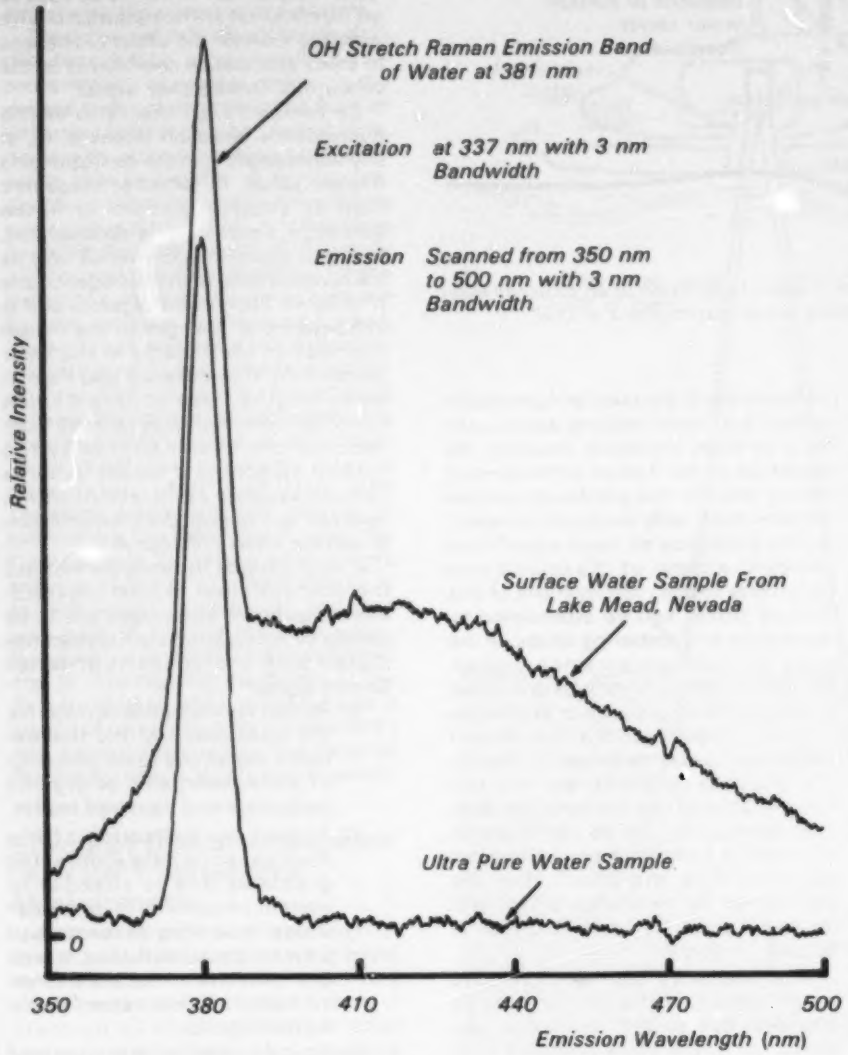

Figure 3. Corrected fluorescence emission spectra for lake and ultra-pure water samples.

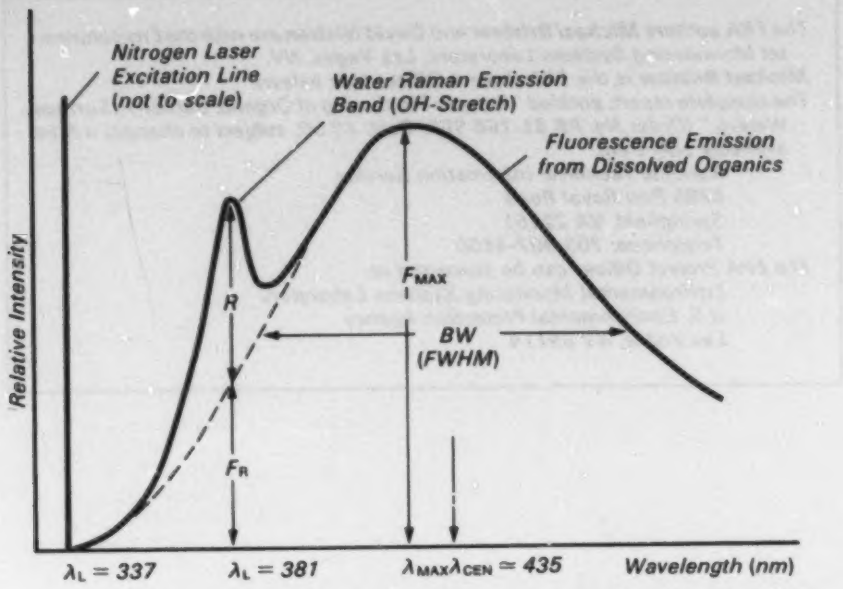

Figure 4. Schematic showing water fluorescence and Raman emission parameters obtained from spectra produced by laboratory spectrofluorometer.

emission spectrum was produced for each water sample, and the six fluorescence characteristics indicated in Figure 4 were obtained in each case. F_{max} is the fluorescence emission intensity at the peak of the spectrum and generally lies in the 415-nm to 440-nm region. R is the peak intensity of the Raman band at 381 nm and F_R is the corresponding fluorescence emission intensity at this wavelength. The other fluorescence spectrum characteristics are BW, the full bandwidth at half height, λ_{max}, the wavelength at the peak intensity, and λ_{cen}, the wavelength at the center of the fluorescence band as determined from the mid-point of BW. A number of fluorescence parameters were then calculated, in particular F_{max}/R and F_R/R, for correlation with independent TOC, DOC and POC measurements obtained on corresponding subsamples.

Conclusions

Important findings of this study that have implications in the design and operation of an airborne laser fluorosensor for monitoring surface water organics are as follows:

(i) It has been shown that the fluorescence data, F_λ, must be normalized using the concurrent water Raman intensity data, R, in order to correct for sample-to-sample variations in optical attenuation and to make the fluorescence data independent of variations in the sensitivity of the laboratory spectrofluorometer. In an airborne laser fluorosensor application, this data correction procedure becomes an absolute necessity because of large variations in optical attenuation that occur from place to place, because of significant variations that can occur with system sensitivity, particularly those involving laser output power, and because of variations in the received fluorescence signal produced by changes in the elevation of the sensor above the water surface. As F_λ and R both exhibit the same dependence on these various phenomena, the ratio F_λ/R becomes independent of these sources of interference.

(ii) The fluorescence signal to Raman signal ratio, F_λ/R, appears to be the fluorescence parameter offering the most promise as a remote sensing indicator of waterborne organic carbon, specifically DOC. The significantly lower correlations between F_λ/R and TOC appear to be due to the variability in particulate organic carbon (POC) concentration in relation to that for DOC in combination with the fact that the POC fraction appears to be less fluorescent than the accompanying DOC. The ability to remotely monitor DOC rather than TOC may be an advantage as the presence of DOC in untreated sources of drinking water is currently generating much concern. In the absence of specific procedures for their removal, natural dissolved organics such as the humic and fulvic acids are able to penetrate through a drinking water treatment plant and undergo conversion into potentially carcinogenic trihalomenthanes during routine chlorination.

(iii) Although F_{max}/R is the version of F_λ/R most highly correlated with DOC, there are compelling reasons for preferring F_R/R as the chosen remote sensing parameter for characterizing surface water organic carbon, particularly as the correlation between F_R/R and DOC was shown to be lower due to interference from an instrumental artifact. First, because both F_R and R and measured at the same wavelength, they are both subject to the same absorption and scattering losses. The same is not true for F_{max}/R, as differential spectral effects were shown to exist between the measurements made at the water Raman wavelength and those made at λ_{max}. The second advantage concerns the fact that, in an airborne laser fluorosensor system employing discrete detector and recording channels for each spectral measurement, the determination of F_R/R requires only three spectral detector channels whereas that for F_{max}/R requires four such channels.

Recommendations

Factors to be considered when designing and operating an airborne

laser fluorosensor for monitoring dissolved organic carbon (DOC) are:

(i) The Raman-normalized fluorescence signal F_A/R should be used in preference to the uncorrected signal F_A as an indicator of DOC.

(ii) The Raman-normalized fluorescence emission measured at the water Raman wavelength, F_R/R, should be used in preference to the maximum value of the Raman-normalized fluorescence emission, F_{max}/R, as the parameter characterizing surface water DOC.

(iii) The airborne fluorescence data should be regarded as a more reliable indicator of surface water DOC than of TOC, because of the unpredictable and relatively non-fluorescent nature of the particulate organic fraction (POC), where TOC = DOC + POC.

(iv) The airborne measurements of F_R/R should be calibrated directly in terms of DOC by making a small number of selected ground truth measurements of DOC on samples collected under the sensor flight path concurrent with the airborne survey.

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__Michael Bristow__ is the EPA Project Officer (see below).
The complete report, entitled "Remote Monitoring of Organic Carbon in Surface Waters," (Order No. PB 81-168 965; Cost: $9.50, subject to change) will be available only from:

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Telelphone: 703-487-4650

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